

The Beginnings of Organic Photochemistry

By Heinz D. Roth*

Although sunlight induced photochemistry must have occurred on the planet Earth for billions of years, the chemical changes caused by light have attracted systematic scientific scrutiny only relatively recently. How did scientists first conceive the idea that the interaction of materials with light could not only cause physical phenomena, but could also alter their chemical nature? When sunlight began to be employed as a heat source for distillation, the eventual discovery of photochemical reactions was assured. One can envision three types of changes that would have aroused the curiosity of laboratory chemists: color changes; the evolution of gas bubbles (oxygen in photosynthesis); and the precipitation of a photoproduct less soluble than its precursor. Less predictable was the observation that sunlight caused crystalline santonin to burst because it is converted into a product with a different crystal lattice. In the course of the eighteenth and nineteenth centuries a variety of photochemical reactions, some observed by chance, others uncovered in carefully planned studies, ultimately led to a major systematic investigation that established photochemistry as a viable branch of chemistry.

1. Introduction

Light induced reactions on this planet are significantly older than life itself. Sunlight induced photochemistry must have literally started as soon as the dust began to settle after the Earth's accretion phase.^[1] The atmosphere of early Earth very likely was essentially free of oxygen. It may have contained chiefly a mixture of hydrocarbons and cyanocarbons, as found on Titan, the largest moon of Saturn.^[2,3] In addition (or instead) it may have contained large quantities of water and carbon dioxide, as found on Mars and Venus, Earth's neighbor planets.^[4] This atmosphere was exposed to radiation from a young Sun, whose spectrum very likely was quite different from the present solar spectrum, with UV fluxes one thousand times greater than the present values.^[1]

Within the first one billion years plant life began to produce oxygen and to build up the atmosphere prevailing today.^[5,6] At the same time it laid the foundation for seemingly inexhaustible energy resources and provided nourishment for higher forms of life. The photolysis of oxygen in the stratosphere generated the protective ozone layer, which would screen human and animal life from the high energy component of the solar spectrum.^[7,8] When *homo sapiens* began to shed his hairy cover, the action of sunlight began to dimerize thymine units of human DNA and cause other changes, leading to skin cancer.^[9] The human body, in turn, developed photoreactivation along with other repair processes.^[9] All these photoreactions have been occurring for aeons without human intervention or, indeed, without being noticed.

How did scientists first conceive the idea that the interaction of materials with light could not only cause physical phenomena, viz. shadows, absorption, reflection, refraction, but could also alter their chemical nature? What kind of a change would be sufficiently noticeable to a chemist to

whom chemical composition and appearance were the chief characteristics of a chemical substance and to whom the notion of "structure" was essentially unknown?

Numerous sunlight induced changes in the general appearance of materials or in their functionality were, indeed, noticed: the bleaching effect, exploited for the manufacture of fibers but detrimental to dyed fabrics; the preservation of oil paintings^[10] and the "chalking" of exterior paint; deleterious effects on beer;^[11] and the spoiling of gun cotton.^[12] Aside from these matters of practical importance, three types of changes can be envisioned to arouse the curiosity of a laboratory chemist: color changes, either temporary (photochromism) or permanent; the development of gas bubbles in a liquid; and the precipitation of a photoproduct that is less soluble than its precursor.

It appears plausible that changes induced in a photochromic dye should have been the earliest photoreactions observed. Indeed, it has been claimed^[13] that *Alexander the Great* exploited such an effect to coordinate the attack of his troops, which proved to be crucial for the outcome of his battles. The Macedonian troops supposedly carried rag bands around their wrists, which were impregnated with a photochromic dye. A color change caused by the exposure to sunlight thus could signal the time of attack. The device has been referred to as Alexander's Rag Time Band.^[13] Alas, no scientific record of the underlying chemistry has been preserved; photochromism wasn't rediscovered until 1876.^[14]

Attempts to utilize the energy of the sun are at least several thousand years old, although the fable of *Phaethon* appears to hint, that man is not meant to achieve this dream.^[*] The burning mirror of *Archimedes* (Fig. 1) may well be the best known early device. More modest uses for laboratory experiments (or their outdoor equivalents) are documented as early as 1599 when *Conrad Gesner* described "The maner of

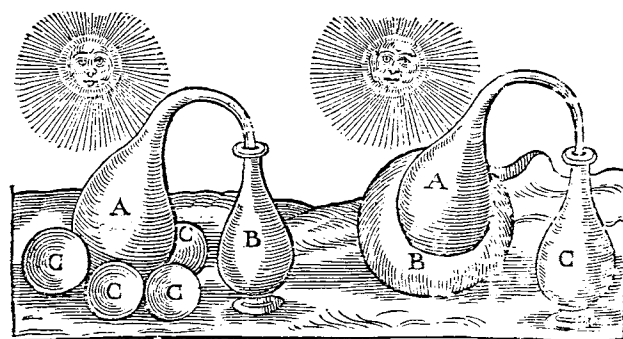
[*] Prof. Dr. H. D. Roth
Department of Chemistry, Wright Riemann Laboratories
Rutgers University
New Brunswick, NJ 08903 (USA)

[*] *Phaethon*, the son of *Helios* and the nymph *Clymene*, tried to drive his father's golden chariot. However, unable to control the powerful steeds, he let the chariot plunge to earth, burning Mt. Oeta and drying the Libyan desert. The entire universe would have perished in the conflagration, had not *Zeus* killed *Phaethon* with a bolt of lightning.



Fig. 1. Burning mirror of *Archimedes*, from "Encyclopedia", Scot, Philadelphia.

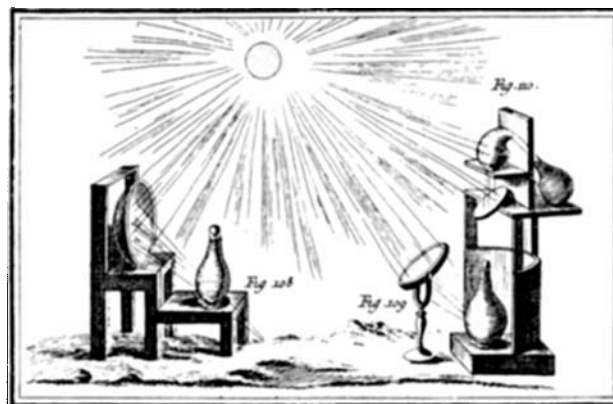
"Distilling in the Sunne" in his monograph on "The practise of the new and old phisicke".^[15] Some fifty years later *John French* showed two setups "to rectify spirits" (Fig. 2), which included provisions for the collection and accumulation of solar radiation, based on the heat capacity of materials such as glass, marble, or cast iron.^[16]



A, Shows the Retort.
B, The Receiver.
C, The Crystal Bowls...

A, Shows the Retort.
B, The Marble or Iron Mortar.
C, The Receiver.

Fig. 2. Two apparatus by *John French* "to rectify spirits" [16].



108. Diffillation ou digestion au soleil par réflexion.
Libav.
109. Diffillation ou digestion par réfraction. Libav.
110. Diffillation au soleil par réflexion pour une corne.
Libav.

Fig. 3. A variety of distillation setups [17].

Less than fifty years later *Libavius* described several methods to focus sunlight on a designated area (Fig. 3). These methods employed mirrors or lenses and suggest an understanding of the principles of optics.^[17] All uses suggested up to *Libavius*' time exploited the heat component of the sun's energy spectrum. Chemical changes were limited to combustion as a result of heating above the point of spontaneous ignition.

2. *Joseph Priestley*— Photochemistry in the Eighteenth Century

It was in a setup, similar to that of *Libavius*, that *Priestley* first encountered a comparably simple chemical conversion. In the course of his experiments on "different kinds of air" he used a twelve inch lens to focus sunlight on a sample of mercury in a closed vessel (Fig. 4).^[18] He observed conversion of the mercury to a red solid with an increase in weight and a diminution of the volume of air. This pioneering experiment was correctly interpreted by *Lavoisier* as a combination of mercury with oxygen, i.e. as an oxidation.^[18] Of course, this conversion is a thermal reaction.



Heinz D. Roth was born in Rheinhausen, in the Lower Rhine region of Germany, in 1936. After completing his formal education at the Universities of Karlsruhe and Köln he received a Dr. rer. nat. degree in Professor Emanuel Vogel's laboratory at the University of Köln with a dissertation on 1,6-methano[10]annulene. After two years as a postdoctoral fellow in W. von E. Doering's laboratory at Yale University he joined the Research Division of (AT&T) Bell Laboratories, Murray Hill, NJ. He has been interested in organic reaction mechanisms, particularly in the structure and reactivity of short-lived radical ions and carbenes; in electron donor-acceptor interactions and photoinduced electron transfer; and in the application of magnetic resonance techniques, especially chemically induced magnetic polarization. Since 1988 he has been Professor of Chemistry at Rutgers University, New Brunswick, NJ. In addition to his main scientific interests he pursues the historical development of the sciences as well as 16th–18th century European cartography.

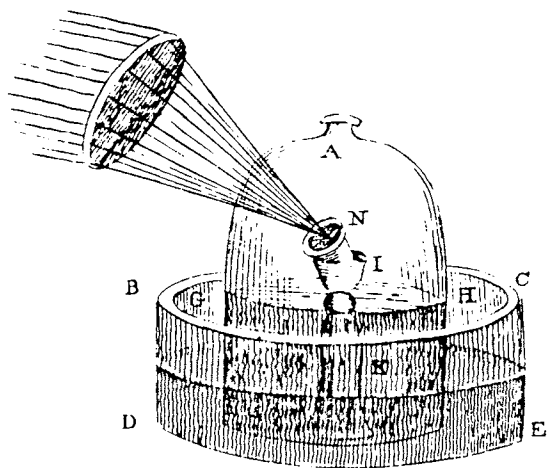


Fig. 4. Apparatus for carrying out calcinations credited to *Priestley* [18]. The metal is contained "in a porcelain cup N, placed upon the stand IK, under a jar A, in the basin BCDE, full of water; the water is made to rise up to GH by sucking out the air with a syphon, and the focus of a burning glass is made to fall upon the metal."



Fig. 5. *Joseph Priestley* (1733–1800), engraving by W. Hall – From a picture by *Gilbert Stewart*. C. Knight, London.

However, *Priestley* also was successful in observing at least two genuine photoreactions in two widely divergent fields: inorganic chemistry and photosynthesis. He exposed partially filled vials of "spirit of nitre" (nitric acid) to sunlight and observed that the liquid assumed a reddish color.^[20] In follow-up experiments he ruled out a thermal reaction and established that the reddish product (nitrogen dioxide) was formed in the vapor phase and then dissolved in the liquid. "Being now satisfied that it was the action of *light* upon the *vapour* of spirit of nitre that gave it colour, I amused myself with throwing a strong light, by means of a lens, into the upper part of a phial, the lower part of which contained colourless spirit of nitre."^[20]

After the initial observation these experiments were obviously well planned and executed. It must be considered the first laboratory photoreaction in the *gas* phase, although this assignment can be made only with all due apologies to its investigator. *Priestley* specifically rejected the term "gas", that had been suggested by the elder (*J. B.*) *van Helmont* (1577–1644), as unnecessary.^[21a]

Priestley (Fig. 5) also deserves credit for first recognizing some facts regarding photosynthesis. In his own words, he "fully ascertained the influence of light in the production of dephlogisticated air (oxygen) in water by means of a *green substance*". When he had first observed the gas evolution, he had explained it as a light-induced reaction of water. However, in later experiments he noticed the presence of *green matter* and a colleague identified tiny plants under a microscope.^[21b]

After learning of *Priestley's* early experiments, *Jan Ingenhousz*, a Dutch physician, who practiced in England and Austria, carried out experiments of his own. He determined that the action of light on plants "improves" air and that *Priestley's* "green matter" must be a plant.^[22] *Nicholas Theodore de Saussure* (1767–1845) resolved the problem in 1804, when he grew plants in enclosed spaces that allowed him to monitor changes in the gas content quantitatively. He demonstrated that the influence of light causes plants to consume water and carbon dioxide and to generate oxygen.^[23]

In concluding this brief overview of *Priestley's* contributions to photochemistry, it is interesting to compare his views of the nature of light with those of his French contemporary *Lavoisier*. *Priestley* considered light a "*chemical principle*" and an "*important agent in the system of nature*", although he conceded that its "effects ... are as yet but little known."^[21b] *Lavoisier*, on the other hand, considered heat and light as agents capable of combining with chemical substances, causing them to expand.

About the more elusive of the two he wrote: "The combinations of light, and its mode of acting upon different bodies are still less known ... it appears to have great affinity with oxygen ..." *Lavoisier* deserves credit for the formulation of many chemical concepts, but the paucity of experimental facts was insufficient to reveal to him the nature of light. His most eloquent statement about light was of a philosophical nature: "By means of light, the benevolence of the Deity has filled the earth with organization, sensation, and intelligence. The fable of Prometheus might perhaps be considered as giving a hint of this philosophical truth even to the ancients."^[24]

3. *J. W. Döbereiner* and the Light Induced Reduction of Metal Ions

An interesting laboratory experiment in photochemistry was carried out by *Döbereiner*. The August 1831 issue of *Pharmaceutisches Central Blatt* (later *Chemisches Zentralblatt*) contains an abstract, which is introduced as follows: "Prof. Döbereiner, dem die Chemie schon so viele interessante Tatsachen verdankt, theilt folgende bemerkenswerthe Beobachtungen über die chemische Wirkung des Lichts mit."^[*] *Döbereiner* exposed an aqueous solution of oxalic acid and iron(III) oxide in a small glass bulb to sunlight. He observed that many tiny gas bubbles developed, which he

[*] "Professor *Döbereiner*, to whom chemistry already owes so many interesting facts, reports the following remarkable observation about the chemical effect of light."

identified as CO_2 , and that a basic iron(II) oxide, humboldtite, precipitated.^[25] With appropriate modifications this reaction has become the basis for ferrioxalate actinometry.^[26, 27]

Döbereiner found similar reductions for salts of Pt, Ag, Ir, and ruled out the corresponding dark reactions by control experiments. However, he missed out on the first photoreaction of a ruthenium compound, because the element that has become the mainstay of so many photochemical studies was not discovered until 1844.

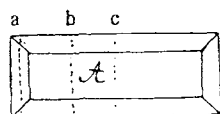
Johann Wolfgang Döbereiner (1780–1849) taught at Jena University and belonged to *J. W. von Goethe's* circle of friends. He made important contributions in several areas: he developed a pneumatic gas lighter; he investigated oxidation reactions with “platinum black”; and he suggested (before *Faraday*) the use of simple galvanic cells for stoichiometric studies. His most important contribution to chemistry was his attempt to order the chemical elements into “triads”. These considerations foreshadowed (and aided) *Mendeleev's* and *Meyer's* work on the periodic table. The photoreduction of metal salts in the presence of oxalate ion appears to have been *Döbereiner's* only excursion into the field of photochemistry.

4. The Photochemistry of Santonin—*Trommsdorff, Sestini, Cannizzaro*

Perhaps the longest known photoreaction of an organic compound is that of santonin, an anthelmintic sesquiterpene lactone. It occurs in the leaves and flower buds of various species of *artemisia* and is the active ingredient of Levant wormseed which was widely used in medicine. It was first isolated in 1830 by *Kahler*^[28] and by *Alms*.^[29] As early as 1834, *Hermann Trommsdorff* reported the curious observation that exposure to sunlight causes santonin to turn yellow, and its crystals to burst.^[30] Several years later, *Heldt* observed these changes under the microscope and was able to determine the directions of the ruptures (Fig. 6).^[31] These

Die Santoninkristalle zerspringen zuerst nach Schnitten, welche normal auf die Längenaxe zugehen; die zugescharften Endflächen werden gleichfalls durch Schnitte abgetrennt, welche die Längenaxe rechtwinklich schneiden. Die Schnittflächen sind keine Ebenen, sie haben sehr unregelmäßige Begrenzungen.

Ist A die Oberansicht eines Krystalls, so zeigen die Linien a, b, c die Richtung der Spaltungsflächen an.



Die abgelösten Stücke zerfallen dann weiter in kleinere, an welchen eine regelmäßige Form nicht mehr erkennbar ist.

Fig. 6. Rupture of santonin crystals upon irradiation, after *Heldt* [1]. “The santonin crystals are cleaved first along cuts normal to the long axis; the inclined crystal faces are also separated along cuts perpendicular to the long axis. The newly created surfaces are not planar but have quite irregular boundaries. If A is the top view of a crystal, the lines a, b, c, indicate the directions of cleavage. The separated pieces are then cleaved further into smaller fragments which no longer show any regular shape.”

experiments are the first dealing with solid state photochemistry.

Trommsdorff came from a well established family of apothecaries; his father (*Johann Bartholomäus*) was an Editor of *Annalen der Pharmacie — Deutsche Apothekezeitung*, which would become *Justus Liebig's Annalen der Chemie*. As an apothecary, *Trommsdorff* had ready access to santonin (or at least to Levant wormseed), and had the skill and the equipment to carry out diligent experiments.

Given this background it may not come as a surprise that *Trommsdorff* was interested in the wavelength dependence of the light induced change, and probed it with the help of a prism. He determined that “Das Santonin wird sowohl durch den unzerlegten, als durch den blauen und violetten Strahl gefärbt... der gelbe, grüne und rothe bringen nicht die mindeste Veränderung hervor”.^{[30][*]} This study must be considered the first to probe the wavelength dependence of an organic photoreaction, a remarkable feat over 150 years ago.

The attempts to characterize santonin and its yellow photoproduct led *Trommsdorff* to the view that these were “two isomeric modifications.”^[30] Similarly, *Heldt*, on the basis of elemental analyses, argued: “White and yellow santonin are identical in their composition, but different in their molecular construction.”^[31] The early workers, of course, did not understand the structures of santonin or its photoproduct.

About twenty years after *Heldt's* publication an Italian chemist began an investigation of santonin, its structure, and its photochemistry.^[32–36] *Fausto Alessandro Sestini* (Fig. 7)



Fig. 7. *Fausto Sestini* (1839–1904), during his year in Pisa. He became director of the Institute of Agricultural Chemistry in 1876 and founded the Institute of Toxicology in 1892. In 1911 his grateful students unveiled a bust in his honor which still graces the hall of the *Faculta Agraria*. *Sestini* introduced *Cannizzaro* to photochemistry and through him, *Ciamician* and *Silber*.

was a teacher in Forli and served as president of the Udine Technical Institute. In 1872 he became director of the agricultural station in Rome and, concurrently, Inspector General for technical education in the Italian Department of Agriculture. In 1876, he accepted a position at the University of

[*] “Santonin is turned yellow not only by the undivided, but also by the blue and violet ray”... whereas... “the yellow, green and red one cause not even the slightest changes.”

Pisa as professor and director of the Institute for Agricultural Chemistry; later he founded an Institute of Toxicology. He was a productive chemist and has many publications to his credit, the majority dealing with agricultural products.

Sestini irradiated santonin in 65% aqueous ethanol and obtained "photosantonin", which he later recognized as a diethyl ester that could be converted into a lactone/acid (photosantonic acid). The latter was prepared directly by irradiation of santonin in 80% acetic acid. These pioneering studies provided the decisive stimulus for Italian photochemistry. When *Sestini* came to Rome, his path crossed that of *Cannizzaro* and he roused his interest in the challenging problems posed by the structure of santonin and its photoproducts. They jointly published one paper,^[33] and in the following years, pursued the problems independently.

Cannizzaro (Fig. 8) and his co-workers confirmed the formation of photosantonic acid and discovered a new photo-

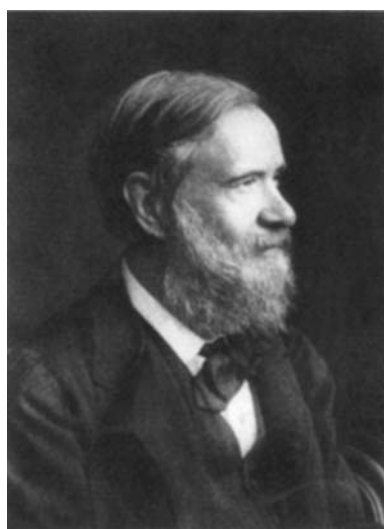
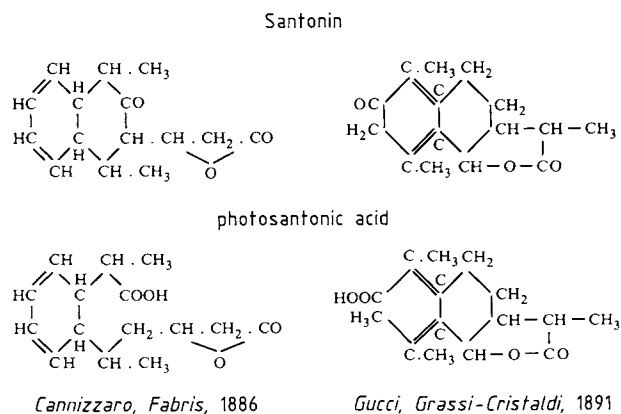


Fig. 8. *Stanislao Cannizzaro* (1826–1910), known for the base induced "disproportionation" reaction of benzaldehyde named after him and for the elegant treatise on molecular theory which he presented at the 1860 Karlsruhe Congress, studied the structures of santonin and two of its photoproducts, photosantonic acid and isophotosantonic acid. In his laboratory *Giacomo Ciamician* first became acquainted with photochemical experiments.

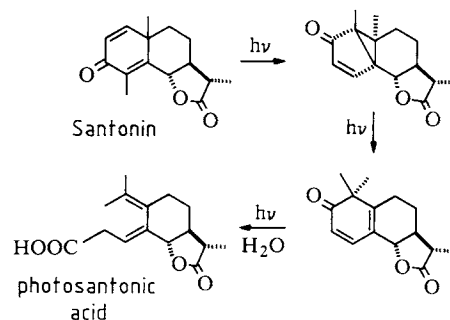
product, which they called isophotosantonic acid.^[37–40] These products were well characterized by their composition, crystal properties,^[41] solubilities, optical rotations,^[42] and by the properties of their salts.^[35] Based on these data *Cannizzaro* recognized the relation of the santonin skeleton to naphthalene, but the correct position of the functional groups in this skeleton eluded him. We illustrate the difficulty of this assignment by the structures proposed by *Cannizzaro* and *Fabris*^[40] in 1886 and by *Gucci* and *Grassi-Cristaldi*^[44] in 1891 (Scheme 1).

Aside from the unusual stereochemistry of the lactone ring, the latter authors assigned a large segment of the structure correctly and only failed to recognize one five-carbon fragment. However, their proposal did not enjoy a better reception than any of the alternative formulations, which deviate more substantially from the correct structure. Organic chemistry simply had not matured to a level that would have allowed an unambiguous assignment. The structural



Scheme 1.

and stereochemical complexity of santonin and the intriguing nature of its photoreactions would continue to puzzle chemists: the structure of photosantonic acid was elucidated only in 1958^[45,46] and the intermediates in its formation were not identified until 1963 (Scheme 2).^[47,48]



Scheme 2.

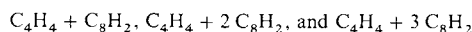
Throughout twenty years of investigating santonin and its photoproducts, *Cannizzaro* always gave *Sestini* credit for the discovery of photosantonic acid, and *Sestini* emphasized his priority.^[34] *Sestini's* importance in the history of photochemistry can hardly be overestimated: he deserves credit for having introduced *Cannizzaro* to light reactions and, through him, *Ciamician* and *Silber*.

5. Early Photodimers— Contributions by *Fritzsche* and *Liebermann*

Among the photoreactions, which first revealed themselves by the precipitation of less soluble products, dimerizations are the chief examples. The earliest laboratory photodimerization was that of anthracene, observed by *Fritzsche* in Petersburg in 1867.

Carl Julius Fritzsche (in the Russian literature *Yulii Fedorovich Fritzsche*, 1808–1871) was a student of *Mitscherlich*. After completing his studies he moved to Petersburg, where he worked for thirty-five years (1834–1869). He was concerned mainly with organic chemical problems, for example he was the first to recognize aniline as a degradation product of indigo. However, he also described the gray modification of tin (tin pest) and deserves credit for his early

work on donor-acceptor complexes. As early as 1857 he had observed and characterized 1:1 molecular complexes of picric acid with benzene, naphthalene, and anthracene.^[49, 50] Remarkably, *Fritzsche* already understood these aromatics as a series of homologs:

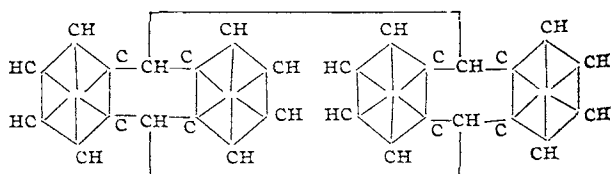


The discrepancy with today's formulation is due to the fact that carbon was assumed to have an atomic weight of six.

Fritzsche carried out detailed investigations of the components of coal tar. During these experiments, he noticed that some tar fractions lost their orange color upon exposure to sunlight. Although no specific reaction was associated with this "bleaching" effect, it is probably best understood as the formation of *endo* peroxides from polycyclic aromatic hydrocarbons. In connection with these experiments, *Fritzsche* noted that anthracene itself was light sensitive. "Gegen das Licht zeigt der Körper $C_{28}H_{10}$ ein sehr merkwürdiges Verhalten. Setzt man eine in der Kälte gesättigte Lösung desselben dem directen Sonnenlichte aus, so beginnt in derselben... die Ausscheidung von mikroskopischen Krystallen..."^[51] Through appropriate control experiments, *Fritzsche* established that he was indeed dealing with a light induced reaction; he also noted that heating above the melting point regenerated anthracene.^[51]

Fritzsche did not speculate in print about the chemical nature of the photoproduct, which he called the "para body". However, his colleague *Butlerov*, in an obituary address commemorating *Fritzsche's* accomplishments, referred to the dimer as an "isomer", probably reflecting *Fritzsche's* thoughts on the subject.^[52] Apparently, this view was shared by a new generation of chemists,^[53] and it prevailed for two more decades.

Twenty-five years after *Fritzsche's* first report *Elbs* recognized the photoproduct as a dimer based on a molecular weight determination^[54] by freezing point depression, a method that had been developed in the 1880's. Subsequently, *Linebarger*^[55] as well as *Orndorff* and *Cameron*^[56] proposed the actual structure (Scheme 3) which has been confirmed by an X-ray diffraction analysis.^[57]



Scheme 3.

Another dimerization reaction was discovered in 1877 by *Liebermann* (Fig. 9) in Berlin. *Liebermann* was familiar with *Fritzsche's* work and, like him, used exposure to sunlight to "bleach coal tar fractions", for example, in the isolation of chrysene.^[58] Thus, the thought that light might cause chemical changes was not foreign to him. While working with

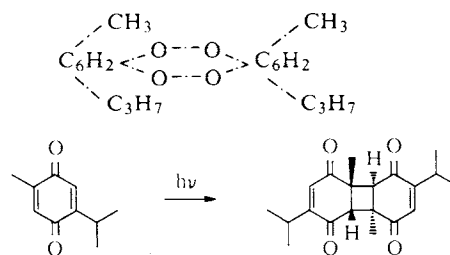
[*] "Towards light the body $C_{28}H_{10}$ shows a strange behavior. When a cold, saturated solution is exposed to sunlight, microscopic crystals begin to precipitate."



Fig. 9. Carl Theodor Liebermann (1842–1914), who elucidated the chemistry of many naphthalene and anthracene derivatives and had a major role in the first synthesis of alizarin as well as its industrial fabrication, carried out a greater variety of photochemical reactions than any other nineteenth century chemist.

thymoquinone, he observed that the yellow crystals under the influence of sunlight turned into a white porcelain-like mass. Through appropriate control experiments he established the conversion as a photoreaction, the first known organic [2 + 2]cycloaddition and a milestone in solid-state photochemistry.^[59, 60] Of course, the elucidation of the exact structure was not achieved until much later.

Liebermann considered the compound a "polymer", a term which, at the time, would have included dimers or trimers. Concerning the structure of the photoproduct *Liebermann* noted that it was cleaved under reducing conditions. He concluded that the quinone molecules were linked through the oxygen atoms,^[60] as shown below (Scheme 4). On the other hand, he had achieved the conversion of the "polymer" into a "polydioxime",^[60] which suggests that the carbonyl groups are free to react and, therefore, cannot be involved in the bonding.



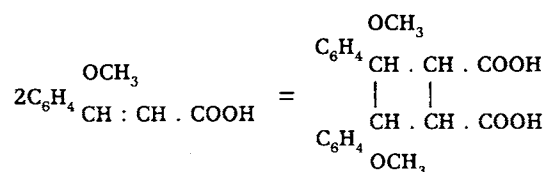
Scheme 4.

One year after *Liebermann's* publication, *Breuer* and *Zincke* reported the isolation of a quinone, $C_{16}H_{10}O_2$, which upon exposure to sunlight gave two different "polymeric" materials.^[61, 62] They did not understand the structure of the quinone, nor the nature of the photoproducts. However, they noted that one of the products readily regenerated the parent quinone upon heating, whereas the second product proved to be more stable. The quinone was later recognized as 2-phenylanthraquinone; the dimers likely

have cyclobutane structures.^[63] A head-to-head dimer might be cleaved more readily than a head-to-tail one.

Liebermann also observed the photodimerization of styrene derivatives. In 1895, he referred to a photochemically generated "polycinnamate".^[64] Also, he found that exposure of cinnamylidenemalonic acid to sunlight converted the yellow substance into a white crystalline product.^[65] He suggested that this reaction was not "simply a stereoisomeric conversion" (*vide infra*) but he failed to recognize the product.

However, the credit for the first dimerization of a styrene derivative clearly belongs to *Bertram* and *Kürsten*, two industrial chemists in Leipzig.^[66] Their work preceded that of *Liebermann* (though narrowly), is further reaching in its understanding, and more definitive in its conclusions. *Bertram* and *Kürsten* were working on the constituents of cassia oil when they noted that β -methylcoumaric acid slowly "polymerized" when exposed to diffuse daylight. Based upon the molecular weight they identified the product as a dimer and also recognized its structure: "this union is likely to occur by mutual saturation of the double bonds." They concluded: "Unter dem Einfluss des Lichts haben sich also zwei Moleküle der β -Methylcumarsäure zu einem Molekül der neuen Säure zusammengelagert. Diese Vereinigung wird wahrscheinlich unter Aufhebung der Doppelbindungen durch gegenseitige Sättigung stattgefunden haben, denn die polymere Säure wird nach dem Behandeln mit Brom, oder nach Einwirkung von Natriumamalgam zum grössten Theile unverändert wieder gewonnen" (Scheme 5).^[67]

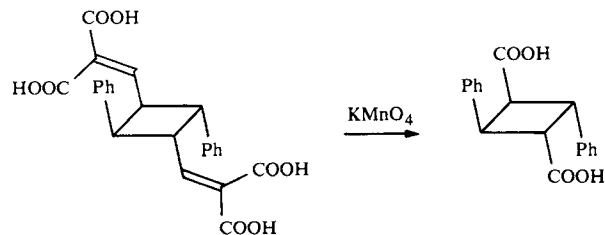


Scheme 5.

They extended their investigation to cinnamic acid and obtained an acid of melting point 274 °C, which they identified as α -truxillic acid.^[66] It is remarkable that these chemists recognized the nature of the dimer, whereas *Liebermann* failed to recognize his "polycinnamate", in spite of his familiarity with truxinic and truxillic acids.

The photoproduct derived from cinnamylidenemalonic acid was recognized by *Riiber*, who reinvestigated this reaction with *Liebermann's* encouragement.^[67] He determined that the product had twice the molecular weight of the diolefin diacid. Permanganate oxidation of the product have rise to α -truxillic acid, establishing structure and stereochemistry (Scheme 6). *Riiber* also succeeded in converting cinnamic acid into (the same) α -truxillic acid^[68] apparently unaware of the earlier work by *Bertram* and *Kürsten*. This earned him a reprimand by *Ciamician* and *Silber*,^[69] who had begun an extensive study of photochemical reactions (see Section 11).

[*] "Under the influence of light, two molecules of β -methylcoumaric acid have associated. This union is likely to occur by mutual saturation of the double bonds; for the polymeric acid is recovered mostly unchanged after treatment with bromide or exposure to sodium amalgam."



Scheme 6.

Carl Theodor Liebermann^[70, 71] spent his entire scientific career in Berlin at the Gewerbeakademie Charlottenburg, which later became the Technische Universität Berlin. In 1863 he was one of the first to join *Adolph Baeyer* as students; he received his doctorate in 1865. Together with *Carl Graebe* he elucidated the structure of alizarin, the active component of the natural dyestuff madder, and carried out the first successful synthesis of this dye with anthraquinone as starting material. This was a significant achievement as it was the first instance of a natural vegetable coloring matter having been produced artificially by a purely chemical method. Subsequently, in 1869, *Caro*, *Graebe*, and *Liebermann* patented a commercially promising procedure; their patent application (BP 1936) was received one day before that of *Perkin's* (BP 1948).^[72, 73]

In 1872, when *Baeyer* was offered the chemistry chair in Strassbourg, an event precipitated by the outcome of the Franco-Prussian War,^[74] *Liebermann* succeeded him in Berlin, and he kept this position until his retirement in 1913 (Fig. 10). He was a founding member of the Deutsche Chemische Gesellschaft and held the office of president for two terms.



C. Liebermann

Fig. 10. The Geheime Regierungsrat *Liebermann*, in later years (after 1900), no longer actively pursued photochemical problems. However, he followed the work of *Ciamician* and *Silber* and exchanged with them unpublished results concerning the isomerization of oximes.

His scientific work is characterized by a wide range of interests. He developed the chemistry of anthracene and many derivatives, he discovered β -naphthylamine, and char-

acterized thiourethane and thiohydantoin and their derivatives. He was especially attracted to natural products occurring in plants, the coca alkaloids foremost among them. During this work he discovered the (*cis*-) stereoisomer of (*trans*-) cinnamic acid and also cinnamic acid crystals of two different crystal structures, without however recognizing them as such! *Liebermann* made several contributions to solution photochemistry, but his most important contributions were solid state photoreactions: the dimerization of quinones^[59, 60] and styrene derivatives.^[64, 65] He also evaluated the efficiency of several artificial light sources.^[65]

6. Geometric Isomerization of Olefins— W. H. Perkin as a Photochemist

Geometric isomerization is one of the most general photoreactions of olefins. The credit for the first observation of this kind, in 1881, belongs to *Perkin* (Fig. 11). He was inves-



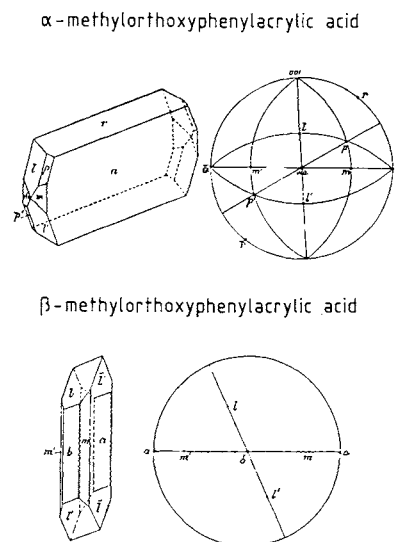
Fig. 11. *William Henry Perkin* (1838–1907), a pioneer of the synthetic dyestuff industry, was the first to observe a light-induced *cis-trans* isomerization.

tigating 2-alkoxycinnamic acids obtained from coumarin and observed the conversion of several “ α -acids” into their “ β -isomers” upon exposure to sunlight.^[75]

Perkin's paper is distinguished by the thorough characterization of these compounds; it contains melting points and boiling points, solubility data, specific gravity at two temperatures, magneto-optical rotation data, refractive indices, and a detailed crystallographic description (Scheme 7). This is the first reference to magneto-optical rotation, which *Perkin* soon developed into an important tool for assigning structures.^[76, 77]

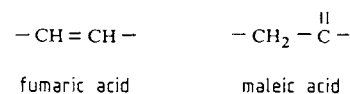
Perkin's paper is also of interest because he pronounced “the cause of isomerization of these bodies... unexplainable”, and continued to discuss fumaric and maleic acid in “traditional” fashion (Scheme 8). Although he definitely was aware of *van't Hoff's* 1874 paper, he apparently did not adopt the new concept of stereochemistry to his system.

Concerning the photochemical content, *Perkin* not only described the light-induced *cis-trans* isomerization, but he also studied the wavelength dependence of the photoreac-



Scheme 7.

tion. In order “to see which rays of light caused the change”, he used “variously colored solutions” as filters, of which he identified “sulphate of quinine” and “ammoniacal sulphate of copper”. He concluded that “the alteration is due to the action of the violet and ultraviolet rays”.^[75]



Scheme 8.

About ten years later *Liebermann* observed similar photoinduced *cis*-to-*trans* rearrangements for cinnamic and several other unsaturated acids.^[78] In the course of these studies one of his coworkers tried “die für Isozimmtsäure so charakteristische Umlagerung durch Jod in Schwefelkohlenstoff”.^[*] This led to greatly accelerated interconversions. A benzene solution of “allo”-cinnamic acid required five months of exposure to produce a 40% precipitation of cinnamic acid, whereas a solution containing iodine required only 12 days for 70% precipitation, a more than tenfold increase in rate. “Allo”-furfuracrylic acid reacted much faster, but the most rapid rearrangement was observed for “allo”-cinnamylideneacetic acid (δ -phenylpentadienoic acid), which required only one minute of exposure to produce a precipitate of the more stable isomer.^[65] *Liebermann* considered the iodine assisted photoinduced isomerization a “general group reaction of the aromatic allo-acids” and suggested the most rapid conversion for a classroom demonstration.^[65]

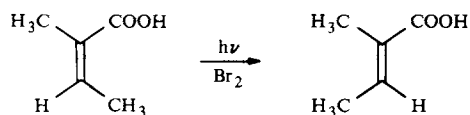
Liebermann's attempts to extend the iodine assisted photoisomerization to nonaromatic unsaturated acids did not meet with success.^[65] However, *Wislicenus* (Fig. 12) achieved this interconversion. Irradiation in the presence of aqueous bromine converted isocrotonic into crotonic acid, angelic into tiglic acid (Scheme 9), and, most rapidly, maleic into fumaric acid.^[79] Although *Wislicenus* is a minor contributor to the development of organic photochemistry, a few remarks about this scientist appear justifiable.

[*] “rearrangement with iodine in carbon disulfide... so characteristic for isocinnamic acid.”



Fig. 12. Johannes Wislicenus (1835–1902), professor at Würzburg and Leipzig Universities, best known for his unsurpassed insight into stereochemical problems. His mechanism for the thermal (and light induced) isomerization of olefins is a classic of mechanistic chemistry.

Wislicenus is best known for his thorough understanding of structural and stereochemical problems. Even before the publications by *van't Hoff* and *LeBel* he had concluded: "Es muss nun unbedingt die Möglichkeit zugegeben werden, dass... bei Körpern von gleicher Strukturformel... doch noch Verschiedenheiten in gewissen Eigenschaften als Ergebnis von verschiedener räumlicher Anordnung der Atome... auftreten können."^{[80][*]}



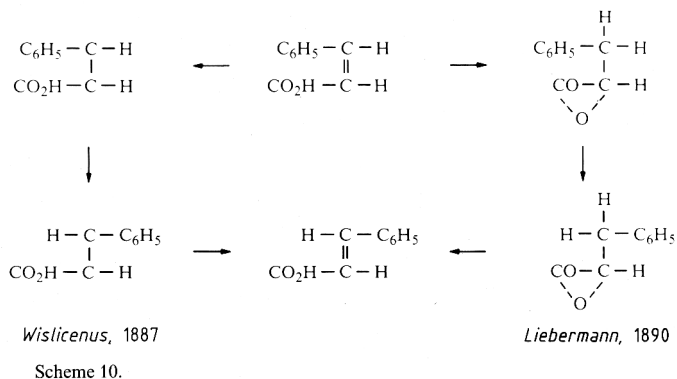
Scheme 9.

In his involvement in photochemistry he showed the same clarity of thought and the skill that characterize his entire work. He recognized that the halogen assisted reactions do not lead to a complete conversion into the more stable isomer, but that the reverse reaction could also occur, resulting in equilibrium mixtures.^[79]

Wislicenus also appears to have had a superb understanding of mechanistic problems. He perceived the mechanism of heat (or light) induced geometric isomerization as follows: "dass durch die zugeführte Energie eine solche Lockerung der doppelten Bindungen eintrete, dass die vorher doppelt gebundenen Kohlenstoffatome vorübergehend dreiwertig werden, in Folge dessen erst eine Wanderung von Atomgruppen, dann die Drehung, und hierauf ein erneuter Zusammenschluss der Kohlenstoffatome stattfindet."^{[81][**]} To the mechanistic chemist of the 1980's this description may lack some details, but on the whole it is quite acceptable (Scheme 10).

[*] "If molecules can be structurally identical, yet possess dissimilar properties, the difference can be explained only by a different arrangement of the atoms in space."

[**] "The added energy causes a weakening of the double bond, so that the formerly doubly bonded carbon atoms become temporarily trivalent. This leads to a migration of groups, then to rotation, and then to renewed bonding of the carbon atoms."



Scheme 10.

Liebmann, on the other hand, considered this mechanism too complicated. As an alternative he proposed^[78] "dass die durch die gesteigerte Energie veranlasste Lockerung der doppelten Bindung dazu führt, dass sie mit Hilfe des Carboxyls tatsächlich gelöst wird, indem dessen Wasserstoff an das eine, dessen frei gewordene Sauerstoffaffinität aber an das andere der vorher doppelt gebundenen Kohlenstoffatome tritt."... "das innere Anhydrid"... gibt... "dann Gelegenheit für die Drehung des Kohlenstoffatoms in die bevorzugte Lage und für die darauf erfolgende Rückbildung der Zimmtsäure."^[*] Quite obviously, this alternative mechanism is of little but historical merit (Scheme 10).

7. Photoinduced Halogenations

In connection with the halogen induced geometric isomerizations of olefins it is of interest to mention briefly the light induced halogenation of aromatic hydrocarbons. These reactions were investigated^[82–85] between 1884 and 1888 by *Julian Schramm* in Lvov, the center of eastern Galicia, which was then a province of Poland.

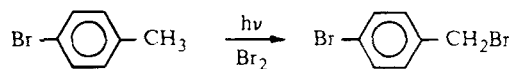
At the time it was recognized that the halogenation products of aromatic hydrocarbons varied with the reaction temperature: bromination of toluene yielded *o*- and *p*-bromotoluene in the cold, but benzyl bromide at elevated temperatures. *Schramm* systematically studied the light induced brominations of alkylbenzenes with normal and branched side chains. In the words of a contemporary reviewer "wirken... Licht bzw. Finsterniss in derselben Richtung wie höhere bzw. niedere Temperatur."^[**] *Schramm* found that direct sunlight or diffuse daylight caused side chain bromination even at low temperatures.^[85]

Schramm apparently had a good knowledge of the chemical literature (which was a somewhat easier task in the 1880's than in the 1980's). He realized that *p*-bromobenzyl bromide had been isolated, though not recognized, as early as 1874 in the light induced bromination of toluene.^[86] *Paul Jannasch*, in *Fittig's* laboratory in Göttingen, tried to improve the poor yield of a dibromo derivative obtained from toluene. Ac-

[*] "... the increased energy causes the weakened double bond to be broken with the help of the carboxyl group, as its hydrogen adds to one and the freed oxygen affinity to the other carbon atom."... "The resulting internal anhydride allows for rotation of the carbon atom into the preferred position and the regeneration of cinnamic acid."

[**] "... light and darkness work in the same way as elevated and low temperatures, respectively."

cordingly, he carried out the bromination "unter gleichzeitiger Einwirkung des directen Sonnenlichts bei Sommertemperatur."^[*] In one of these experiments^[86] he obtained crystals of m.p. 63°C which *Schramm* recognized as *p*-bromobenzyl bromide (Scheme 11).



Scheme 11.

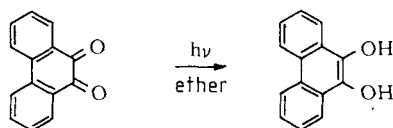
Schramm also foresaw the commercial potential of photohalogenations: "Hoffentlich wird die Methode geeignet auch zur fabrikmäßigen Darstellung der genannten Produkte."^{[83][**]} Eventually, this expectation became reality: photochlorinations have long been exploited commercially, although the reactions discovered by *Schramm* are not of industrial interest today.

8. Heinrich Klinger— the Photoreduction of Carbonyl Compounds

Aside from the dimerization of quinones, which is observed mainly in the solid state, photoreductions must be considered the principal light-induced reactions of quinones in solution. The credit for having observed and investigated the first reactions of this type belongs to *Heinrich Klinger*, who originated his work in *Kekule's* institute in Bonn during an investigation of isobenzil, an assumed isomer of the long-known diketone. In an attempt to produce the supposed isomer from a solution of benzil in ether, he observed the slow precipitation of a crystalline material. However, this result was not always reproducible.^[87, 88]

Among the pioneers of photochemistry, *Klinger* is the only one who relates the puzzled frustration of an experimental chemist dealing with an unknown variable and faced with seemingly irreproducible results. After "many time-consuming experiments" he finally noticed that "some of the tubes were exposed to direct sunlight in the morning hours".^[88] He identified the crystals as a molecular complex of two moles of benzil with one mole of benzoin and concluded that "sunlight causes a partial reduction of benzil dissolved in wet ether".^[88]

Having recognized the reducing action of sunlight on benzil, *Klinger* carried out analogous experiments with phenanthrenequinone with similar results (Scheme 12). He also began to investigate the role of the solvent and he reported the existence of preliminary results for benzoin, nitro compounds, several quinones, fuchson, etc. *Klinger* first report-



Scheme 12.

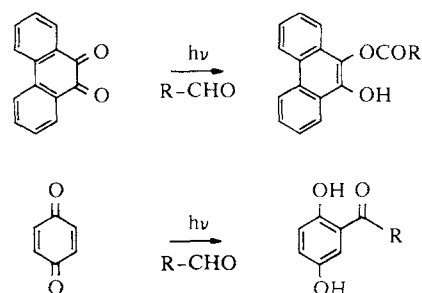
[*] "...at summer temperatures under simultaneous exposure to direct sunlight."

[**] "Hopefully, this method could prove suitable for the industrial preparation of these products."

ed these results in preliminary form in *Sitzungsberichte der niederrheinischen Gesellschaft für Natur- und Heilkunde* in 1883 and 1885;^[87] he formally published them in *Berichte* in 1886.^[88] There is very little doubt that *Klinger* had priority over *Ciamician* (see Section 9), albeit by a narrow margin.

Two years later he reported an interesting extension of his work. When he replaced the ether by acetaldehyde "um dadurch die Arbeit des Sonnenlichts gleichsam zu erleichtern"...^[*] he observed: "Die Wirkung des Lichts ist ...eine ganz eigenartige, synthetische, wie sie... bisher nur in der lebenden Pflanze beobachtet wurde;... als die beiden Substanzen sich zu einer Verbindung vereinigen, in welcher das Chinon als reducirt, der Aldehyd dagegen als oxydirt erscheint."^{[89][**]} The product observed in this light-induced reaction, monoacetylphenanthrenehydroquinone, was indeed a new type of photoproduct.

Klinger extended the reaction to a series of aldehydes and ketones and also investigated alternative quinones. The reaction of benzoquinone with benzaldehyde proved to be particularly interesting.^[90, 91] The product isolated in this reaction, 2-benzoylhydroquinone (or 2,5-dihydroxybenzophenone), established an interesting variation of the phenanthrenequinone derived product (Scheme 13). *Klinger* re-



Scheme 13.

ferred to these reactions as "Synthesen durch Sonnenlicht" (syntheses by sunlight); he must be considered the first to have exploited photochemical methods for synthetic purposes. He perceived these reactions as similar to the photosynthesis of the living plant.^[90-92]

To probe this similarity further he investigated the wavelength dependence by using aqueous solutions of inorganic ions as filters, including cuprous ammonium sulfate and potassium dichromate solutions. He noted that the photochemical response of the quinones was most pronounced in the blue region, whereas green plants showed optimum response in the red region of the spectrum.^[89]

Although the photoreactions discovered by *Klinger* give rise to products that appear to be widely different, it is clear that their formation is initiated by a common mechanism. The photoexcited quinone reacts with the various substrates by hydrogen abstraction, and the resulting radicals form the isolated products by recombination, disproportionation, or by free radical addition or abstraction.

Heinrich Konrad Klinger (1853-1945) studied in Leipzig and Bonn and received a doctorate in 1875 in Göttingen as

[*] "...to facilitate the work of the sunlight."

[**] "The effect of light is a strange synthetic one... with precedent only in the living plant... as the two compounds are joined to form one, in which the quinone appears reduced but the acetaldehyde oxidized."

UEBER DIE
EINWIRKUNG VON PHOSPHORPENTACHLORID
AUF
PHENYLOXAMINSÄUREÄTHYLÄTHER
UND
PARATOLUYLOXAMINSÄUREÄTHYLÄTHER.

INAUGURAL-DISSERTATION
ZUR
ERLANGUNG DER PHILOSOPHISCHEN DOCTORWÜRDE
AN DER
UNIVERSITÄT GÖTTINGEN
VORGELEGT VON
HEINRICH CONRAD KLINGER
AUS
LEIPZIG

LEIPZIG,
DRUCK VON BREITKOPF UND HÄRTEL
1875.

Fig. 13. Title page of *Heinrich Klinger's* thesis, Leipzig, 1875

a student of *O. Wallach*. It is an interesting coincidence that *Klinger* received his doctorate (Fig. 13) in Göttingen in the same year in which *Jannasch*^[86] published his light-induced experiments. We do not know whether *Klinger* knew of this work, whether he interacted with *Jannasch*, or even met him at all. He had carried out his thesis work in Bonn and received his degree in Göttingen only because his mentor had moved there.

Klinger returned to Bonn, where he rose to direct the pharmaceutical chemistry branch. In 1896 he accepted a call or, more correctly, followed a ministerial order to Königsberg (Fig. 14), where he served as director of the pharmaceutical laboratory and professor of chemistry. Following his retirement in 1922, he lived to the age of almost 92. He died on March 1, 1945 in East Prussia during the destructive climax of World War II.

9. Ciamician and Silber—an Early Episode

It was in *Cannizzaro's* Istituto Chimico della Regia Università in Rome that *Ciamician* and *Silber* were first introduced to photochemical reactions. It would have been hard to overlook an effort involving . . . “one kilogram of santonin dissolved in 52 liters of acetic acid . . . exposed to sunlight in several bottles”.^[40] Nevertheless, their interest was aroused only slowly. When they joined *Cannizzaro's* group in 1881, they first focussed their attention on pyrrole chemistry. They produced a sizeable body of work, which earned *Ciamician* the Gold Medal of the Regia Accademia dei Lincei in 1887.

In the summer of 1885 *Ciamician* (Fig. 15) began some photochemical experiments^[93, 94] and the following year *Silber* joined in the investigations.^[95] *Ciamician* “insolated”

Ministerium
der geistlichen, Unterrichts- und Medicinal-
Angelegenheiten.

Bonn, den 16. October 1895.

21.
2266. K

WI 012 22656 I

Ihr Befehl zur in meinem Auftrage mit
Ihren gezeichneten Berufsbefehlungen
beurtheilt, Sie aufzugeben sind, auf
nicht nach Königsberg i. Pr. zu begeben und
falls der beabsichtigten vorübergehenden
Dr. Spigatus in der Abwesenheit der gegen
unzeitlich gezeichneten Unterschrift sind in
der Absicht der gegenzeitlich gezeichneten
Laboratoriums bis auf Weiteres zu verhalten.
Für diese Fortsetzung bewillige ich
Ihnen vom 20^{ten} October d. J. ab eine
Remuneration von jährlich
3000 Mark,
in Worten: Dreitausend Mark, welche
Ihnen die Königlich-Preussische
Königsberg i. Pr. in vorübergehender
Funktion im Voraus zahlen wird. Dergleichen
gibt die Königlich-Preussische
Bonn ungenügend, Ihre
An
der Königlich-Preussischen
Laboratorium
zu
Bonn.

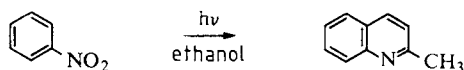
Fig. 14. Excerpt from the letter notifying *Klinger* of his reassignment to Königsberg. “Pursuant to negotiations carried out with you on my behalf you are ordered herewith to proceed to Königsberg i. Pr. with the utmost dispatch to substitute Professor Dr. *Spigatus*, currently on leave of absence, in executing pharmaceutical chemistry instruction and in directing the Pharmaceutical Chemical Laboratory until further notice. For these services I grant you a remuneration of 3000 Mark annually, beginning October 20th . . .”



Fig. 15. *Giacomo Ciamician* (1857–1922), during his early years in Bologna.

(exposed to sunlight) alcoholic solutions of benzoquinone. After five month's exposure he observed conversion into hydroquinone and acetaldehyde. The following year *Silber*

exposed an alcoholic solution of nitrobenzene. This reaction produced aniline and acetaldehyde, but the exceptionally skilled *Silber* also found evidence for the formation of 2-methylquinoline (quinaldine, Scheme 14).



Scheme 14.

These were interesting and promising results, and the two investigators must have had every intention to follow up these early findings. However, their first engagement in photochemical research was not destined to be of extended duration. The limitation of their initial efforts had its roots in the custom of nineteenth century chemistry that allowed a researcher to “reserve” a field for continued investigation. Most respectable scientists honored such a claim (chemistry has indeed come a long way in the last one hundred years).

After reporting his first results in the *Rendi conti della Regia Accademia dei Lincei* on January 3, 1886,^[93] *Ciamician* became aware of *Liebermann's* 1885 publication.^[60] He must have considered the potential overlap between *Liebermann's* solid state photodimerization and his own photoreduction in solution and must have been satisfied that these two areas were sufficiently different. He rushed his work to publication in the *Gazzeta Chimica* “per acquistare il diritto di continuare le mie ricerche intraprese. . .”^[*] even though he had not yet proven that the observed redox reaction was indeed a photoreaction (“That the conversion is indeed caused by light will be ensured by repeating the experiment in the dark”).^[94] However, before *Ciamician's* *Gazzeta* paper was reviewed in *Berichte*, *Klinger's* work on the reaction of phenanthrenequinone appeared, in which *Klinger* claimed this area of research for himself, including specifically the photoreduction of nitrobenzene.^[88]

There is very little doubt that *Ciamician's* experiments in Rome were carried out independent of *Klinger's* studies in Bonn. The *Rendi conti* publication^[93] appeared only a few months later than *Klinger's* *Sitzungsbericht* of 1885.^[87b] Nevertheless, *Ciamician* and *Silber* honored *Klinger's* claim graciously. They sent a brief summary of their preliminary work to *Berichte*; it contained the previously missing control experiment for the benzoquinone photo-reduction and a brief account of the nitrobenzene reduction. They announced that, for the time being, they would not pursue the subject any further and concluded: “Wir sehen mit grossem Interesse den Resultaten der weiteren von Hrn. *Klinger* in Aussicht gestellten Untersuchungen entgegen.”^{[95][**]}

We do not know whether they took this action readily or whether they may have been persuaded by *Cannizzaro*, who had been elected to honorary membership in the Deutsche Chemische Gesellschaft in 1873. The fact remains that *Ciamician* and *Silber* did not publish another photochemical paper until fourteen years later. It also is obvious that *Ciamician* and *Silber*, having obeyed research etiquette themselves, expected similar consideration. Their major body of

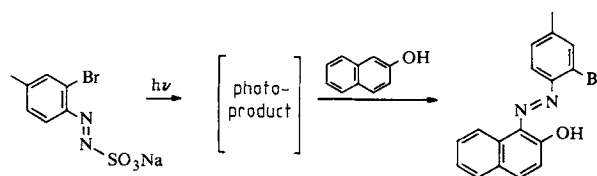
[*] “. . . to ensure the unencumbered continuation of my research.”

[**] “We are looking forward with great interest to the results of the further experiments delineated by *Klinger*.”

photochemical work in the early 1900's contains several quick rebuttals and some polemics, particularly against *Ciamician's* compatriot *Paterno*.

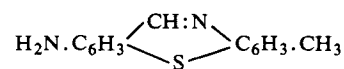
10. Photochemistry of Diazo and Diazonium Compounds

Because of their practical importance as photoresist materials and their significance as precursors for divalent-carbon species, it appears appropriate to discuss briefly the photo-reactions of diazo compounds and of the somewhat related diazonium salts. This class of compounds became accessible through the pioneering studies of *Peter Griess* beginning in 1858.^[96] Although it is not clear when their sensitivity to light was first noticed, attempts to utilize them for the purpose of imaging are documented as early as 1889. *Adolf Feer* noticed that irradiation of diazonium sulfonates, R–N=N–SO₃Na, in the presence of phenolates or arylamines led to the formation of azo dyes, presumably via the free diazonium ion. After a film containing these reagents was exposed, unreacted diazonium sulfonate could be removed by washing, leaving a colored negative (Scheme 15).^[97]



Scheme 15.

Only a year later, *Green, Cross* and *Bevan* received a patent for a process generating a positive image based on the fact that irradiation converts the diazo compounds of “dehydrothiolumidine” (primulin) into products incapable of coupling. After exposure, an image could be “developed” by converting the unreacted diazonium compound to an azo dye with an appropriate reagent (Scheme 16).^[98]



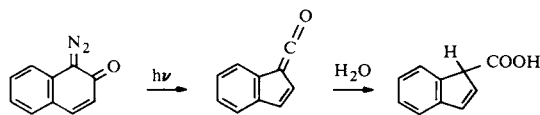
Scheme 16.

It is indicative of the progress of photochemistry that in 1890 *Green* and colleagues no longer considered mere light sensitivity noteworthy. They were concerned with the practical exploitation of this property: “Von den zahlreichen Verbindungen, welche lichtempfindlich sind, erfüllen nur wenige die Bedingungen zur Erzeugung eines photographischen Bildes. . .”^{[98][*]} Other imaging systems were proposed by *Andresen*,^[99] *Schön*,^[100] and *Ruff* and *Stein*.^[101]

Diazoketones have been known since 1881 when *Schiff* prepared diazocamphor,^[102] and by the turn of the century several such compounds were known.^[103, 104] However, commercial application in diazo-type manufacture became possible only after *Kögel* and *Neuenhaus* had introduced ap-

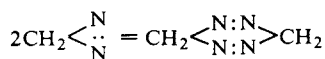
[*] “Among the many compounds that are light sensitive only a few meet the requirements for generating a photographic image. . .”

appropriately substituted “naphthoquinone diazides” (1-diazo-naphthalene-2(1*H*)-ones).^[105] The nature of their photo-products and the course of the reaction was elucidated by *Oscar Süss*,^[106] who recognized that these materials undergo Wolff rearrangement with loss of nitrogen and ring contraction, generating a ketene. Reaction with adventitious water produces a carboxylic acid which can be removed by an alkaline wash (Scheme 17). The application of this photochemistry for positive photoresist materials has become a multimillion dollar industry.



Scheme 17.

Concerning other diazo compounds, despite their pronounced light sensitivity, their photoinduced decomposition was not discovered until early in the 20th century. Several diazo compounds were synthesized in the 1880's.^[107–109] For example, ethyl diazoacetate was prepared by *Curtius* in 1883,^[107] diazomethane was obtained by *von Pechmann* in 1894,^[110] neither publication mentions any light-induced reactions.



Scheme 18.

The first reference to the irradiation of diazomethane appeared in 1901 when *Hantzsch* and *Lehmann* reported that the action of sunlight upon the diazo compound generates dihydrotetrazine (Scheme 18).^[111] This interesting claim was corrected when *Curtius* et al. found only nitrogen, ethylene, and a very low yield of a greasy residue.^[112] Although this paper must be considered an early report on poly(m)ethylene, it stimulated neither polymer nor carbene chemistry. We ascribe this fact to the lack of appreciation for the unique nature of divalent-carbon intermediates and to a failure to understand the relation between diazo compounds and carbenes.

11. Conclusion

At the end of the nineteenth century photochemistry was but a modest facet of the exciting and rapidly expanding science of chemistry. The principal contributors studied photochemical problems only as an aside to the work for which they were (and still are) best known. Only a limited number of reactions were known, and the sun was virtually the exclusive light source; its light was used unfocussed and unfiltered.

Only *Liebermann* experimented with alternative light sources, particularly with an arc lamp, a gas burner with a metal oxide mantle, and a magnesium flame; his results were far from promising.^[65] *Trommsdorff* had evaluated the wavelength dependence of a photoreaction with the help of a prism,^[30] *Perkin*^[75] and *Klinger*^[89] used filter solutions.

Perkin also mentions an experiment in which “light was concentrated on...” a sample, an obvious reference to a focussing device.^[75]

On the other hand, several of the general reaction types known today had been encountered. When *Liebermann* discovered the iodine mediated photoisomerization of olefins, he subjected a representative cross section of then known photoreactions to the newly found reaction conditions.^[65] He surveyed three dimerizations and one rearrangement, but did not refer to abstraction or transfer reactions, such as those studied by *Klinger* and *Ciamician*; the fourth general reaction type, photocleavage, had yet to be discovered.

Organic photoreactions were being utilized for the purpose of imaging,^[97–101] and *Klinger* et al.^[89–91] and *Schramm*^[85] had pointed out, respectively, the preparative and industrial prospects of photochemistry. All these facts suggest that the time was ripe for an outstanding scientist who would devote a major effort to organic photochemistry and establish it as a major scientific discipline.

With the advent of the twentieth century *Ciamician* (Fig. 16) and *Silber* began a systematic investigation of photochemical reactions. Their achievements far surpassed any

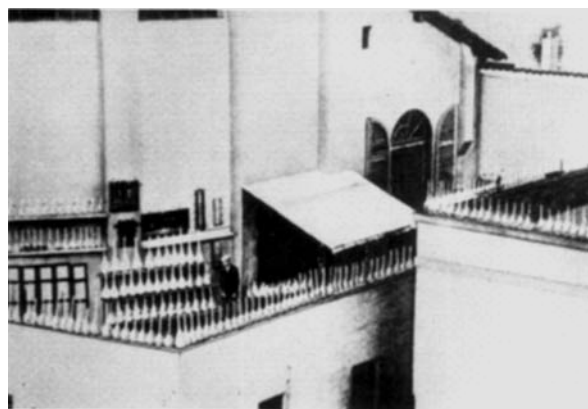


Fig. 16. *Ciamician* in his “laboratory”, on the roof of the chemistry building in Bologna. The Dipartimento di Chimica “G. Ciamician” in the Via Selmi in Bologna is a fitting memorial to this pioneer of photochemistry.

previous effort and established photochemistry as a major branch of chemistry. In particular, they provided many examples of ketone photochemistry: in addition to photoreductions (vide supra) they discovered photopinacolization, intramolecular cycloadditions, and both α - and β -cleavage. These systems would later prove to be of great importance for the development of molecular photochemistry, as they revealed many fundamental principles, for example, the concepts of singlet and triplet as well as n,π^* and π,π^* states.

Ciamician and *Silber* reported their findings in two parallel series of thirty-seven publications entitled “Azione Chimiche della Luce” in *Gazzetta Chimica Italiana* and “Chemische Lichtwirkungen” in *Berichte der deutschen chemischen Gesellschaft*. These papers deal with an astonishing variety of systems and document unmatched skills in the separation of sometimes complex product mixtures, unprecedented understanding in the identification of the components, and unparalleled insight into the nature of photo-

chemical reactions. However, *Ciamician's* crowning achievement was the truly astonishing lecture he delivered before the International Congress of Applied Chemistry in New York in 1912. Under the title "The Photochemistry of the Future" he summarized the status which photochemistry had attained in little more than a decade chiefly through his and *Silber's* efforts and revealed his prediction of its future. He emphasized particularly the utilization of solar energy which he deemed second only to nuclear energy.^[113] We note that *Ciamician* is not the first to have entertained the thought of solar energy conversion. *Swift* described *Gulliver's* encounter with a Lagadoan academician "upon a project for extracting sunbeams out of cucumbers"^[114] and *Goethe's* Faust yearned for "Bäume, die sich ewig neu begrünen", a task, incidentally, which Mephisto thought achievable: "Ein solcher Auftrag schreckt mich nicht, mit solchen Schätzen kann ich dienen".^[115] Of course, *Ciamician* was the first to put this dream on a rational basis. It is a testimony to *Ciamician's* vision that more than three quarters of a century after his prophetic lecture the promise of harvesting solar energy has yet to be fulfilled.

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